Hydrophilic and hydrophobic superparamagnetic Fe_3O_4 nanoparticles as T_2-contrast agents for oil reservoir applications

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Abstract

Information acquisition and analysis of oil reservoirs are one of the most challenging and scientifically demanding areas in the oil exploration industry. Herein, we report a single-step solvothermal method for the synthesis of highly-stable hydrophilic and hydrophobic superparamagnetic iron oxide nanoparticles (SPIONs) as T_2-contrast agents for oil reservoir applications. Hydrophilic and hydrophobic characteristics on the surfaces of SPIONs were achieved using polyethylene glycol (PEG-400) and oleylamine (OLA) for water/oil phases of the reservoir, respectively. For comparison, uncoated SPIONs were also prepared by coprecipitation method using NH_4OH as a reducing agent. Stability of hydrophilic SPIONs was monitored in deionized (DI) water and/or artificial seawater (ASW), while stability of hydrophobic SPIONs was investigated in model oil (cyclohexane-hexadecane 1:1). X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) profiles confirm the magnetite (Fe_3O_4) phase of synthesized nanoparticles (NPs). The presence of C−O (532.4 eV) and $-NH_2$ (399.7 eV) in XPS spectra of N1s and O1s substantiate the surface functionalization of Fe_3O_4 NPs with PEG and OLA, respectively. Transmission electron microscopy (TEM) images demonstrate the spherical shape NPs having particle diameters 11.6 ± 1.4, 12.7 ± 2.2 and 9.1 ± 3.0 for PEG-Fe_3O_4, OLA-Fe_3O_4, and Fe_3O_4, respectively. NMR T_2-relaxation measurements were performed first time by an acorn area analyzer to demonstrate meaningful results for targeted reservoir applications. The transversal relaxivity (r_2) values for PEG-Fe_3O_4 (66.7 mM^{-1} s^{-1}) and OLA-Fe_3O_4 (49.0 mM^{-1} s^{-1}) were 2.07 and 1.53 times higher than Fe_3O_4 (32.2 mM^{-1} s^{-1}) NPs, respectively. The observed (i) quenching of T_2-relaxation signals with SPION concentration, (ii) excellent relaxivity properties due to their ultra-small size, and (iii) long-term stability in different media, suggest them to be promising T_2-contrast agents for oil reservoir applications.

Key Words: Hydrophilic; Hydrophobic; Superparamagnetic; Magnetite; Oil reservoir.

1. Introduction

One of the most challenging, globally significant and scientifically demanding areas in the oil exploration industry is the information acquisition and analysis of oil reservoir [1]. Over the last decade, NMR spectroscopy has been used in the petroleum industry as a complementary tool to characterize oil formations during the exploration stage. NMR is also applied to examine the various types of fluids present in the pores of reservoir rocks [2]. By tuning the NMR probe to a resonant frequency, allows specific regions of the reservoir rocks can be imaged. This approach relies on the fundamental NMR technique known as spin-spin relaxation (T_2-relaxation) in which the transverse component of the magnetization vector exponentially decays towards its equilibrium position: there are various factors which can influence the T_2-relaxation time. For instance, the viscosity of a fluid is inversely related T_2 [3], which is an important parameter for oil the exploration industry to investigate the in-situ molecular dynamics of petroleum fluids. Moreover, the concentration and size of superparamagnetic NPs [DEFINE THIS ABBREVIATION] also plays a significant role to alter T_2-relaxation, which gives negative enhancement (i.e., darker image) in T_2-weighted magnetic resonance imaging (MRI).

Superparamagnetic iron oxide nanoparticles (SPIONs) have shown their potential applications in the fields of magnetic storage [4, 5], catalysis [6, 7], electrocatalysis [8, 9] and biomedicine such as targeted drug delivery [10, 11], hyperthermia treatments [12, 13] as well as T_2-contrast agents for MRI [14, 15]. Recently, SPIONs have also been investigated as T_2-contrast agents for reservoir applicationa [16]. The word "Contrast" means the signal differences between adjacent regions, e.g. ‘tissue/bone,' and ‘tissue/vessel' for medical applications and ‘oil/water' in terms of reservoir applications. Typical contrast agents for computed tomography and X-rays display contrast enhancements due to electron-density differences. On the other hand, contrast agents for MRI

show contrasting effects based on their interactions with neighboring protons [17]. It is well-known that MRI is based on NMR in which relaxation of proton spins occurs in the presence of applied magnetic field. Therefore, contrast agents should have the capability to shorten the relaxation time of the neighboring protons [17]. It is reported that T_1-based agents provide positive contrast enhancements (i.e., brighter image) in T_1-weighted MRI, whereas, T_2-based agents deliver negative contrast enhancements (i.e., darker image) in T_2-weighted MRI [17, 18]. Moreover, the efficiency of contrast agents is usually expressed in terms of longitudinal (r_1) and transversal (r_2) relaxivity. The higher values of r_1 and r_2 are related to the T_1-positive and T_2-negative contrast enhancements, respectively [19].

Among various forms of iron oxides, magnetite (Fe_3O_4) NPs exhibit variety of potential applications owing to a high Curie temperature (T_C^{bulk} ~850 K at $T_V \approx$125 K) and highest saturation magnetization of (M_S^{bulk} ~92 emu/g) among the oxides of iron [20]. Moreover, the magnetic behavior of magnetite NPs is can related to their size. It is well-established that magnetite NPs show transition from multi-domain to single-domain magnetic structures as the size decreases below 90 nm [THIS NEEDS A REFERENCE]. Upon further reduction in the size to below 30 nm, these NPs reveal superparamagnetic behavior at room temperature [21]. Significantly, if the size of NPs $\geq$ 30 nm, then the coercive forces dominate and can cause aggregation in the presence of strong external magnetic fields [22]. However, the synthesis of stable and dispersible SPIONs having ultra-small size is very challenging and hence distinct research efforts are required to prepare SPIONs of desirable properties for MRI applications.

Various synthetic methods, i.e., coprecipitation [23], solvothermal [24, 25], hydrothermal [22, 26], polyol [27, 28], thermal decomposition [29] and thermolysis [30] have been adopted for the synthesis of hydrophilic and hydrophobic SPIONs. Magnetite NPs coated with silica shell (Fe_3O_4@SiO_2) have

been prepared via a modified Stober process using Fe_3O_4 seeds [31]. It was observed that the silica shell thickness could be controlled by tuning various experimental parameters, i.e., the concentration of seeds, the ratio of tetraethyl orthosilicate (TEOS)/Fe_3O_4 and reaction termination time. The synthesized NPs exhibit superparamagnetic behavior at room temperature. Similarly, Fe_3O_4@SiO_2 having hydrophilic characteristics were synthesized by thermolysis using poly (vinyl pyrrolidone) (PVP), and TEOS in the presence of NH_4OH catalyst [30]. Nevertheless, these synthetic processes involve tedious surface treatments and multi-step procedures in which the hydrolysis and condensation reaction of TEOS occurs.

Recently, Abbas et al. [27] reported single-step polyol method for the synthesis of hydrophilic SPIONs using polyethylene glycol (PEG) as a solvent as well as a stabilizing agent. The pH of the solution was adjusted to ~10 by the addition of NaOH and reaction was carried out at a relatively higher temperature (300 ^oC). They also reported a modified polyol method for the encapsulation of silica shell on the surface of magnetite NPs to induce hydrophilicity under similar reaction conditions [28]. Using another appoach, Xu and his co-workers [29] reported single-step thermal decomposition method for synthesis of monodisperse hydrophobic SPIONs in which the size of NPs was tuned by varying the volumetric ratio between oleylamine (OLA) and benzyl ether. The thermal decomposition of iron acetyl acetonate $Fe(acac)_3$ was carried out in the presence of highly flammable benzyl ether at high temperature (300 ^oC), which can be a quite hazardous procedure. From the above discussion, it is anticipated that PEG could act as a reducing and stabilizing agent, which induce hydrophilic characteristics. Similarly, OLA can also act as a mild reducing as well as a stabilizing agent, however, it induces hydrophobic characteristics on the NPs surface under control reaction conditions.

In this work, we present a novel, single-step, facile solvothermal method for the synthesis of functionalized SPIONs in which the solvents (PEG-400, OLA) act as reducing, stabilizing and capping agents. PEG-400 and OLA were selectively employed to provide hydrophilic and hydrophobic functionalities on the surface of SPIONs, respectively. For comparison, uncoated-Fe_3O_4 NPs were also prepared by a coprecipitation method using NH_4OH as precipitating agent. Several physicochemical techniques were engaged in characterizing the synthesized SPIONs. The stability of functionalized SPIONs was monitored in their respective environment. The quenching of T_2-relaxation signals with the concentration of SPIONs was determined. The functionalized SPIONs exhibited excellent relaxivity properties which promote their ability to work as promising T_2-contrast agents for oil reservoir applications.

2. Experimental

2.1 Synthesis of hydrophilic SPIONs

The hydrophilic magnetite (Fe_3O_4) NPs were prepared by the solvothermal method using PEG-400 (Aldrich). Briefly, 6 mmol (2.185 g) of iron(III) acetylacetonate $Fe(acac)_3$ (97%, Fluka) and 75 g of PEG-400 were mixed with the help of Silverson mixer (L5M-A, USA) in 125 mL polytetrafluoroethylene (PTFE) vessel for 1 h to obtain a homogenous red suspension at room temperature. The PTFE vessel was placed in a stainless steel autoclave reactor (Parr, USA) and kept in a synthetic oven (280A, Fisher Scientific) at 180 °C for 24 h. Then, the mixture was cooled down to room temperature, and the black slurry of Fe_3O_4 was precipitated by the addition of absolute ethanol (>99%, Fisher Scientific) with an excess amount of diethyl ether (>99%, Sigma-Aldrich). The NPs were centrifuged at 10,000 rpm for 10 min using 3-30KS centrifuge (Sigma, Germany). To remove unbound PEG-400, the NPs were redispersed in absolute ethanol and centrifuged again at 20,000 rpm for 30 min. The purification procedure was repeated three-times.

The final black product was labeled as **PEG-Fe_3O_4** and divided into two equal parts. Then, half of the product was dispersed in Milli-Q water while remaining half was dried in vacuum oven at 50 ^oC for 24 h.

2.2 Synthesis of hydrophobic SPIONs

The hydrophobic Fe_3O_4 NPs were synthesized by the solvothermal method using OLA (70%, Aldrich). Briefly, 5 mmol (1.820 g) of $Fe(acac)_3$ precursor and 25 mL of OLA were mixed with the help of Silverson mixer in 125 mL PTFE vessel for 1 h to obtain a homogenous red suspension. The PTFE vessel was placed in a stainless steel autoclave reactor and kept at 280 °C for 24 h. Then, the mixture was cooled down to room temperature. The precipitation and purification procedure of the synthesized NPs remained same as described above for the synthesis of hydrophilic Fe_3O_4. The final black product was labeled as **OLA-Fe_3O_4** and divided into two equal parts. Then, half of the product was dispersed in cyclohexane-hexadecane (1:1) mixture, while the remaining half was dried in vacuum oven at 50 ^oC for 24 h.

2.3 Synthesis of uncoated SPIONs

The uncoated-Fe_3O_4 NPs were prepared by coprecipitation of Fe(III) and Fe(II) in the molar ratio (2:1) using NH_4OH solution as a reducing agent. The complete reaction was carried out under an Ar atmosphere, and the stirring was carried out by using overhead Teflon stirrer (IKA Eurostar, Germany). In a typical procedure, 100 mL of Milli-Q water was acidified with 1.0 mL of concentrated HCl (37%, Sigma-Aldrich) and purged with Ar gas for 15 min. Then, 1.2 M $FeCl_3.6H_2O$ (>99%, Sigma-Aldrich) and 0.6 M $FeCl_2.4H_2O$ (>99%, Sigma-Aldrich) aqueous solutions were prepared in acidified water. The solutions were filtered-off with 0.2-micron hydrophobic PTFE membrane filter (Millex-FG, Millipore). Then, Fe(II) solution was mixed dropwise with Fe(III) solution in a three-neck round bottom flask. The reaction mixture was heated

up to 80 ^{o}C and 20 mL of NH_4OH (28−30%, Sigma-Aldrich) solution was poured into the iron precursors at 500 rpm. The color of dispersion was changed from golden brown to black indicating the formation of Fe_3O_4 NPs. The dispersion was continuously stirred, refluxed and heated for 1 h followed by the addition of 5 mL tetramethylammonium hydroxide (25%, Sigma-Aldrich) solution to stabilize the NPs. Then, allow the reaction mixture to cool down to room temperature. The magnetic NPs were washed several times with absolute ethanol as described above. The final product was labeled as **Fe_3O_4** and divided into two equal parts. Then, half of the product was dispersed in milli-Q water while remaining half was vacuum dried in the oven at 50 ^{o}C for 24 h.

2.4 Functionality and colloidal stability test

The functionality and colloidal stability of hydrophilic SPIONs were tested in deionized (DI, pH ~7.0) water as well as artificial seawater (ASW, pH ~8.0); ASW was prepared which meets American standard for testing and materials (ASTM). Briefly, ASW "ASTM D1141-98" standard was prepared by dissolving 36.03 $g.L^{-1}$ of a salt mixture in DI water. The composition of salt mixture was as follows; NaCl (99.5%, 24.53 g), $MgCl_2$ (98%, 5.20 g), Na_2SO_4 (99%, 4.09 g), $CaCl_2$ (99.9%, 1.16 g), KCl (99%, 0.695 g), $NaHCO_3$ (99.7%, 0.201 g), KBr (99%, 0.101 g), H_3BO_3 (99.5%, 0.027 g), $SrCl_2$ (99.9%, 0.025 g) and NaF (99%, 0.003 g). The estimated density and salinity of ASW were 1.020 $g.mL^{-1}$ and 36.0 $g.L^{-1}$ respectively. Similarly, the functionality and colloidal stability of hydrophobic SPIONs was monitored in standard model oil composed of the mixture of cyclohexane and hexadecane (1:1). The as-synthesized SPIONs were dispersed in each bottle containing the model oil and ASW (1:1). Then, the functionality of SPIONs was investigated before applying an external magnetic field, while the stability of synthesized SPIONs was observed after applying the magnetic field. [RE-WRITE THIS IT IS UNCLEAR WHAT WAS DONE]

2.5 Material characterization

The diffraction patterns of various SPIONs were recorded using a Smart Lab X-ray diffractometer (Rigaku, Japan) with a diffraction angle (2θ) range of 15−80° at a scan rate of 2°/min. Surface analysis of the synthesized magnetic materials was performed using an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Scientific, UK). The thermal behavior of functionalized NPs was studied using differential scanning calorimeter (DSC 204 F1 Phoenix, NETZSCH, Germany). DSC measurements were performed in the temperature range 20−500 °C with a scan rate of 10 °C/min under N_2 environment to avoid material oxidation. The surface morphology, size, and shape of the synthesized SPIONs were evaluated by using a field emission scanning electron microscope (FESEM-Tescan Lyra-3) as well as a transmission electron microscope (JEM-2100, JEOL, USA). TEM grids were coated by putting slurry of the analyte onto 200 mesh copper grids. The grids were examined after 1 h of degassing [ADD MORE DETAIL – HOW WAS IT DONE?]. An inductively coupled plasma atomic emission spectrometer (ICP-AES, Varian) was used to estimate the Fe content in as-synthesized SPIONs. To determine the feasibility of contrast agents, T_2-relaxation curves for various concentrations of SPIONs were attained using acorn area analyzer (Xigo Nanotools, UK), which is normally used for surface area measurements [ADD A REFERENCE]. For all the measurements, values of tau (τ) and the total number of scans were kept constant, i.e., $\tau = 0.5$ ms, scans = 4.

3. Results and discussion

3.1 Functionality and colloidal stability of synthesized SPIONs

The functionality and colloidal stability of SPIONs have key importance for their ultimate use in oil exploration industries for reservoir applications. Fig. 1A demonstrates functionality testS of (a) PEG-Fe_3O_4, (b) OLA-Fe_3O_4, and (c) Fe_3O_4 in an oil-DI water environment. The partitioning

observed by naked eye shows that PEG-Fe_3O_4 and Fe_3O_4 NPs have hydrophilic characteristics due to the presence of PEG and OH surface functional groups, respectively. The presence of OH groups on the surface of Fe_3O_4 NPs is expected due to the hydroxylation process during coprecipitation [32]. Moreover, OLA-Fe_3O_4 NPs remain in the oil-phase owing to the presence of OLA functionality, which induces surface hydrophobicity.

The colloidal stability of as-synthesized SPIONs was monitored in mixed oil-DI water and oil-seawater phases. Fig. 1(A) demonstrates the stability of (a, d) PEG-Fe_3O_4, (b, e) OLA-Fe_3O_4, and (c, f) Fe_3O_4 in the oil-DI water phase. It was observed that PEG-Fe_3O_4 and OLA-Fe_3O_4 NPs remained stable and attracted in an external magnetic field in their respective environment. However, the uncapped-Fe_3O_4 NPs became unstable and were not fully attracted after applying the magnetic field. This is because the Fe_3O_4 NPs are pH-dependent and their surfaces are easily oxidized to other forms of iron oxides/hydroxides in aqueous media having pH $\leq$ 7 [33]. Similarly, Fig. 1(B) depicts the stability of (a, d) PEG-Fe_3O_4, (b, e) OLA-Fe_3O_4, and (c, f) Fe_3O_4 in oil-seawater phases. Similar behavior was experienced by PEG-Fe_3O_4 and OLA-Fe_3O_4 NPs. Importantly, the uncapped-Fe_3O_4 NPs became stable and attracted after applying a magnetic field in ASW due to slightly basic nature of seawater (pH ~8.0).

3.2 Crystal structure, phase, and chemical composition analysis

The phase, purity and crystal structures of as-synthesized SPIONs were examined via XRD analysis. Fig. 2 shows the diffractograms of three type of magnetic NPs synthesized using PEG, OLA, and NH_4OH. The observed diffraction profiles are consistent with the standard pattern (JCPDS card no. 65-3107) indicating the formation of pure magnetite phase [34, 35]. The six major diffraction peaks observed at 2θ positions of 30.08°, 35.50°, 43.22°, 53.65°, 57.13° and 62.75° assigned to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) crystalline planes, respectively [34,

[35]. According to structure analysis, the magnetite NPs exhibit the cubic inverse spinel structure with *Fd-3m* space group [36]. The comparison of XRD profiles reveals that peak intensities decrease after surface functionalization of magnetite NPs due to the amorphous nature of capping agents (PEG-400 and OLA), which may indicate the coating of SPIONs [37]. The average crystallite sizes of magnetite NPs as evaluated using Debye−Scherrer equation [38] were found to be ~13.3, ~14.1 and ~9.6 nm for PEG-Fe_3O_4, OLA-Fe_3O_4, and Fe_3O_4, respectively. The cubic unit cell parameters (a) and cell volume (V) for as-synthesized NPs are reported in Table 1. The comparison indicates that PEG-Fe_3O_4 and OLA-Fe_3O_4 have almost similar values of unit cell parameters, perhaps owing to the same synthetic protocol (solvothermal method). However, the uncapped-Fe_3O_4 NPs synthesized via the co-precipitation method possess lower unit cell parameters. This difference of values indicates that synthetic protocols play a pivotal role in controlling the crystal structure of NPs [22]. It is well-documented that magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) exhibit almost similar XRD patterns [39]. Therefore, the phase analysis of as-synthesized SPIONs was further explored via XPS technique, which exclusively determines various phases of iron oxides, i.e., magnetite, maghemite, and hematite.

A survey of PEG-Fe_3O_4, OLA-Fe_3O_4, and Fe_3O_4 spectra (Fig. 3a) shows the presence of Fe2p, N1s, O1s, and C1s features. The observed spectral lines are labeled according to their binding energies. For C1s, the adventitious/aliphatic carbon (C−C) peak detected at 284.8 eV was used as a reference. Fig. 3b shows XPS profiles of PEG-Fe_3O_4, OLA-Fe_3O_4, and Fe_3O_4 freshly synthesized powder samples. The observed spectra are almost similar to each other as well as with the standard Fe_3O_4 sample [40]. It is reported elsewhere that Fe $2p_{3/2}$ does not have a satellite peak for Fe_3O_4 phase [23, 26, 40]. Similarly, the absence of satellite peak at 719.0 eV here further confirms the magnetite phase of as-synthesized iron oxide NPs. Moreover, the two distinct asymmetric

peaks observed at binding-energy values of 710.6 and 724.1 eV (spin-orbit splitting, Δ = 13.5 eV) corresponded to $Fe2p_{3/2}$ and $Fe2p_{1/2}$ further confirm Fe_3O_4 phase (711.0 and 724.6 eV in the case of γ-Fe_2O_3 phase) [40].

3.3 Surface functionalization

The presence of hydrophilic and hydrophobic coating on the surface of SPIONs was investigated using two complementary techniques: XPS and DSC. The XPS profiles also give evidence for the presence of an amorphous coating on the surface of the NPs. The presence of amine ($-NH_2$) groups in XPS spectrum of OLA-Fe_3O_4 indicate surface functionalization of the NPs. It is reported that the binding-energy values corresponding to bonded amines are observed in the range 398−400 eV [41]. A symmetric peak with low intensity detected at 399.7 eV in the N1s spectrum (Fig. 3c) attributed to $-NH_2$ group of OLA in which nitrogen is coordinated with metal oxide NPs [42]. The observed binding-energy is consistent with the literature value for amine-capped NPs [41, 43]. Figs. 3(d-f) reveal the deconvoluted high-resolution XPS spectra of the O1s component for PEG-Fe_3O_4, OLA-Fe_3O_4, and Fe_3O_4, respectively. Two characteristic peaks observed in all O1s spectra at ~530.0 and ~531.6 eV belong to Fe−O of iron oxide NPs core [22] and hydroxyl group (−OH) [44], respectively. Additionally, a strong shoulder peak detected at 532.4 eV in O1s profile of PEG-Fe_3O_4 (Fig. 3d) assigned to C−O group of PEG-400 in which oxygen atoms are bonded to aliphatic carbon [44, 45]. The existence of Fe−O and C−O confirms the surface functionalization of Fe_3O_4 NPs with PEG groups.

DSC was further employed to investigate the organic surface coating, thermal stability and phase transformations of the magnetite NPs at elevated temperature. Fig. 4 shows the thermal behavior of uncoated and coated SPIONs in the temperature range of 20–500 °C. From the DSC curve of uncoated-Fe_3O_4, it is quite clear that the NPs are almost thermally stable and no phase

transformation is observed up to 500 ^{o}C under an N_2 environment. However, a small exothermic process observed in the temperature range 125–200 °C could be attributed to the removal of hydroxyl (−OH) groups adsorbed during coprecipitation on the surface of uncoated-Fe_3O_4. In the case of coated NPs (PEG-Fe_3O_4 and OLA-Fe_3O_4), DSC curves show multi-step exothermic processes in the range of 150–400 °C with maxima at 279 and 275 °C, which are attributed to the decomposition of organic capping agents, i.e., PEG-400 and OLA fractions, respectively [46, 47]. The observed thermal behavior of PEG-Fe_3O_4 and OLA-Fe_3O_4 confirm the functionalization of SPIONs.

3.4 Surface morphology and particle size analysis

Surface morphology and particle size of as-synthesized SPIONs were investigated via FESEM and TEM techniques. High and low-resolution FESEM images of (a) PEG-Fe_3O_4, (b) OLA-Fe_3O_4, and (c) Fe_3O_4 are shown in Fig. 5 and S1, respectively. From the micrographs of PEG-Fe_3O_4 and OLA-Fe_3O_4, it can be clearly observed that the synthesized SPIONs have almost a spherical shape and single distribution. However, aggregation and lumps have been observed in the case of uncapped-Fe_3O_4 NPs synthesized by the coprecipitation method, as indicated by red circles in Fig. 5(c). The comparison indicates that the solvothermal protocol allows control of shape and size of NPs as compared to the coprecipitation method. Spherical shaped NPs are predominantly formed in the synthesis of Fe_3O_4 owing to the low surface area per unit volume, and hence minimum surface free-energy [48]. It is because, the nucleation rate per unit area is isotropic at the NP interfaces, which results in minimization of surface free-energy [48]. Therefore, the equivalent growth rate in all directions of nucleation leads to the formation of spherical NPs.

High and low-resolution TEM images of (a) PEG-Fe_3O_4, (b) OLA-Fe_3O_4, and (c) Fe_3O_4 are shown in Fig. 6 and S2, respectively. The images clearly indicate that PEG-Fe_3O_4 and OLA-

Fe_3O_4 NPs exhibited spherical morphology and homogenous distributions, whereas uncoated-Fe_3O_4 NPs exhibit irregular shapes. The average particle diameter of as-synthesized NPs is 11.6 ± 1.4, 12.7 ± 2.2 and 9.1 ± 3.0 for PEG-Fe_3O_4, OLA-Fe_3O_4, and Fe_3O_4, respectively (Table 1). The broad distribution observed for uncapped-Fe_3O_4 NPs indicates that the particle size was not well-controlled with the coprecipitation method. The comparison also indicates that particle diameters estimated from TEM images are consistent with average crystallite sizes observed from XRD. The selected area electron diffraction (SAED) patterns of (d) PEG-Fe_3O_4, (e) OLA-Fe_3O_4, and (f) Fe_3O_4 SPIONs (Fig. 6) are consistent with XRD profiles (Fig. 2) and literature [46]. The SAED patterns also exhibit structural homogeneity and a high degree of crystallinity of the synthesized NPs. The patterns are indexed based on cubic inverse spinel structure with *Fd-3m* space group and unit cell parameters of magnetite NPs (Table 1).

3.5 Growth mechanism of SPIONs

The possible growth mechanism of these as-synthesized SPIONs is proposed below. The PEG-400 and OLA can be considered high-boiling solvents playing three roles (reducing, stabilizing, and capping agents) in the solvothermal synthesis of SPIONs. The mechanism of Fe_3O_4 NPs formation may become more complicated when metal-organic salts $Fe(acac)_3$ are used as precursors. At the elevated temperature, $Fe(acac)_3$ precursor decomposes and liberate Fe^{3+} ions. PEG-400 and OLA are oxidized at high temperature and generate electrons reducing Fe^{3+} to Fe^{2+}. PEG-400 being a stronger reducing agent generates Fe_3O_4 NPs at relatively low temperature (180 ^oC), whereas OLA, being a mild reducing agent generates the NPs at a relatively higher temperatures (280 ^oC). These organic solvent/additives effectively control the particle growth and prevent aggregation. Spherical shaped NPs are predominantly formed due to the minimum surface free-energy as described above (Section 3.4) [48]. However, the synthesis of SPIONs by the

coprecipitation method using Fe^{3+} and Fe^{2+} ions is pH-dependent based on the following chemical reaction [33],

$$2\ Fe^{3+} + Fe^{2+} + 8\ OH^{-} \rightarrow Fe_3O_4 + 4\ H_2O \qquad (1)$$

According to above equation (1), a complete co-precipitation of Fe_3O_4 NPs was observed for pH above 7, whilst also keeping the molar ratio (2:1) between Fe^{3+} and Fe^{2+} under a non-oxidizing environment. In this case, pH was adjusted to ~9.0 using NH_4OH as a precipitating agent and the NPs were stabilized with tetramethylammonium hydroxide solution.

3.6 T_2-relaxation and relaxometric studies

Spin-spin relaxation NMR (T_2-relaxation) measurements were performed to investigate the possibility employing these SPIONs as T_2-contrast agents for oil reservoir applications. The measurements were carried-out for various concentrations of Fe in the as-synthesized SPIONs (Fig. 7). Before T_2-measurements, the Fe contents present in the samples were estimated with the help of ICP-AES analysis; being 57.9, 61.5 and 68.8 wt.% of Fe content for PEG-Fe_3O_4, OLA-Fe_3O_4, and Fe_3O_4, respectively. For this purpose, six various concentrations of Fe (mM), i.e., 0.012, 0.024, 0.060, 0.12, 0.24 and 0.48 were prepared to see the relaxometric properties of hydrophilic and hydrophobic samples in ASW and model oil, respectively.

T_2-relaxation measurements of (a) PEG-Fe_3O_4, (b) OLA-Fe_3O_4, and (c) Fe_3O_4 SPIONs with respect to Fe concentration are shown in Fig. 7. The significant quenching of T_2-relaxation signals was observed with increasing concentration of SPIONs. For comparison, T_2-relaxation curves and relaxation times of pure DI water, ASW, cyclohexane, hexadecane, and model oil are also provided in Fig. S3. The relaxation process took place due to energy exchange between neighboring protons in solvent molecules. SPIONs induce inhomogeneity in the presence of an

applied magnetic field, which results in de-phasing of magnetic moments of protons and leads to the quenching of the T_2 signal. The decrease in T_2-relaxation time with Fe concentration indicates that these NPs can act as promising T_2-contrast agents for oil reservoir applications.

The relaxivity properties were investigated by plotting various Fe concentration (mM) against relaxation time ($1/T_2$, s^{-1}), as shown in Fig. 7d. The r_2 value can be estimated from the slope of equation (2) [49].

$$1/T_2 = 1/T_2^o + r_2\,[Fe] \qquad (2)$$

Where, T_2, T_2^o, r_2, and [Fe] are the relaxation time of NPs dispersion, pure solvent, transversal relaxivity and iron concentration (mM).

The inverse of relaxation time ($1/T_2$) can also be expressed in terms of relaxation rate (R_2). The estimated r_2 values [SHOULD IT BE r2 OR R2??? CHECK AND CORRECT EVERYWHERE] were found to be 66.7, 49.0, and 32.2 $mM^{-1}\ s^{-1}$ for PEG-Fe_3O_4, OLA-Fe_3O_4, and Fe_3O_4 SPIONs respectively. The higher r_2 values for PEG-Fe_3O_4 and OLA-Fe_3O_4 indicate that the capped-Fe_3O_4 show excellent relaxivity properties owing to their higher dispersion in the respective media as compared to uncapped-Fe_3O_4. The estimated r_2 values are competitive with the commercial contrasting agents such as SHU-555C (r_2 = 69 $mM^{-1}\ s^{-1}$) and 10 times higher than Gd-DTPA (r_2 = 5.3 $mM^{-1}\ s^{-1}$) [19]. Moreover, the comparison of various T_2-contrast agents is provided in Table 2. The outcomes suggest that theses functionalized SPIONs can be effectively used as T_2-contrast agents for reservoir applications due to their excellent relaxivity properties.

Table 2 Comparison of various T_2-contrast agents for MRI applications.

Sample composition	Synthesis method	Colloidal stability	Particle size (nm)	Field strength (T)	r_2 (mMs^{-1})	Refs.
Fe_3O_4	Polyol	H_2O, PBS	8	1.5	82.7	[50]
USMIO-Fe_3O_4	Coprecipitation	H_2O	6.6	0.47	33.9	[51]
MION-Fe_3O_4	Coprecipitation	---	4.6	---	34.8	[52]
USPIO-Fe_3O_4	Coprecipitation	0.9 % saline	4.9	0.47	53.1	[53]
US-Fe_3O_4	Coprecipitation	pH: 5.3-8.5	4.6	7	64.4	[23]
US-Fe_3O_4	Coprecipitation	pH: 5.3-8.5	2.2	7	28.6	[23]
PEG-Fe_3O_4	Solvothermal	H_2O, seawater	11.6	1.5	66.7	This Work
OLA-Fe_3O_4	Solvothermal	H_2O, seawater	12.7	1.5	49.0	This Work

US: Ultra-small, MIO: Magnetic iron oxide, PIO: Paramagnetic iron oxide, PBS: Phosphate buffered saline.

4. Conclusion

In summary, highly-stable hydrophilic and hydrophobic SPIONs contrast agents were successfully prepared using a single-step solvothermal method. Hydrophilic and hydrophobic characteristics were induced on the surfaces of the magnetite NPs by adsorbing either PEG-400 or OLA, respectively. The additives (PEG-400 and OLA) played three roles, i.e., as reducing,

stabilizing, and capping agents during the synthesis processes. The hydrophilic and hydrophobic SPIONs were found to be stable in ASW and model oil, respectively which is the key requirement for the harsh oil reservoir environment. The magnetite phase having cubic inverse spinel structure with *Fd-3m* space group was confirmed by XRD. The surface functionalization of capped-NPs was established by the presence of C−O and $-NH_2$ groups in XPS spectra. TEM images demonstrated the spherical shape of as-synthesized NPs having ultra-small diameters < 15 nm, which is a suitable size for passing through reservoir rock cores. The suitability of NMR T_2-relaxation as a measurement tool, i.e., acorn area analyzer as demonstrated here for the first time. It can be seen that meaningful results can be obtained by this miniaturized technique, showing its potential for targeted reservoir applications. The significant quenching of T_2-relaxation signals was observed with increase in concentration of the SPIONs. The values of r_2 were found to be 66.7, 49.0, and 32.2 mM^{-1} s^{-1} for PEG-Fe_3O_4, OLA-Fe_3O_4, and Fe_3O_4 SPIONs respectively. The observed excellent relaxivity properties due to their ultra-small sizes and long-term stability in the respective medium show these hydrophilic and hydrophobic SPIONs to be promising T_2-contrast agents for oil reservoir applications. Additionally, overt the long-term with improved functionalization and surface chemistry, these contrast agents have great potential as MRI imaging agents and nanosensors for remote interrogation to develop next generation technologies for reservoir applications. [THIS SECTION NEEDS TO BE EDITED WITH ADDED REFERENCES, AS I HAVE EXPLAINED TO YOU BEFORE – AS IT STANDS IT IS INADEQUATE – YOU NEED TO FOLLOW THE GENERAL GUIDANCE I GAVE FOR YOUR LAST PAPER]

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